Chemistry and Materials Research
ISSN 2224- 3224 (Print) ISSN 2225- 0956 (Online)
Vol.6 No.10, 2014
www.iiste.org

Quantum Mechanical Study of the Kinetics, Mechanisms and Thermodynamics of the Gas-Phase Pyrolysis of Isopropyl Bromide

Adeboye, Omolara Olubunmi
Chemistry Department, Emmanuel Alayande College of Education, P.M.B. 1010, Oyo, Nigeria
*E-mail of corresponding author: moadeb5848@yahoo.com

Abstract
Computational studies of the kinetics, mechanisms and thermodynamics of the gas-phase pyrolysis of isopropyl bromide at 623K was studied using PM3 in the semi-empirical and DFT with B3LYP at 6-31G* level methods of calculation. The reaction proved to be a unimolecular reaction and followed a first order rate equation. The calculation showed that the pyrolysis of isopropyl bromide proceeds through a four-membered cyclic transition state which involved a C_8-H_{11} and C_4-Br_6 bond breaking and H_{11}-Br_6 bond making. The Arrhenius parameters, log A (13.6 and 13.8) obtained for both methods are in good agreement with experimental result (13.6).
Keywords: semi-empirical, isopropyl bromide, gas-phase, kinetics.

1. Introduction

The presence of C_β – H on the alkyl side of an organic halide such as hydrogen bromide, chloride and iodide gives gas–phase elimination through a four–centered cyclic transition state mechanism. Gas–phase unimolecular reactions appeared to take place through a 4-centered and 6-centered cyclic activated complex ((O'Neal and Benson, 1967). Hydrogen halide elimination from the alkyl halides to produce olefins is usually four centered reactions. This reaction involves Markovnikov's addition reaction which goes through a four - centered transition states. The main aim of this study is to use semi-empirical and density functional computational approach in SPARTAN to predict the kinetics, thermodynamics and the mechanism of the thermal decomposition of isopropyl bromide (Fig 1).

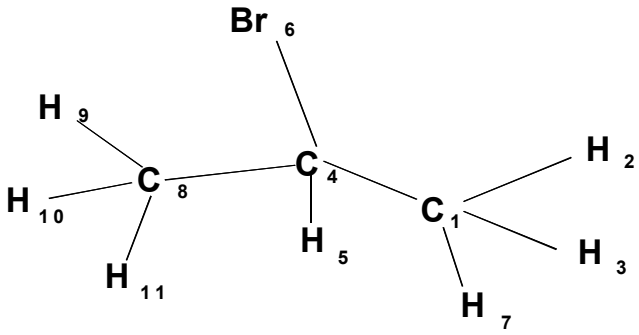


Fig 1: Geometry of Isopropyl Bromide

Semi-empirical PM3 and MP2/6 31G* level calculations were performed on methyl oxalyl chloride; it was observed that the mechanism implies a concerted non- synchronous process and the kinetic and thermodynamic parameters were in good agreement with the experimental method (Tania *et al.,* 2004). The gas-phase elimination kinetics of several methyl ω – chloroesters using *ab-initio* and DFT method was studied. It was discovered that the mechanism suggest a planar concerted, non-synchronous four-membered cyclic transition state to give methyl acrylate and the calculated kinetics and thermodynamic parameters agrees well with experimental values (Romero *et al.,* 2009). The kinetics and mechanisms of the gas-phase elimination of 2-hydroxyphenethyl chloride and 2-methoxyphenethyl chloride appears to proceed through a three-membered cyclic transition state by the anchimetric assistance of the aromatic ring and through a free-membered cyclic transition state (Brusco *et al*., 2009). Adejoro *et al*., 2013 studied the kinetics, mechanisms, thermodynamics and vibrational spectroscopy of the pyrolysis of ethyl bromide in the gas – phase at 623K using HF at 3-21G, 6-31G* and DFT with B3LYP/6 31G*, 6-311++G (2df, 2p) basis sets. It was discovered that the calculated result are in agreement with experimental result. Elimination of several ω –bromonitrile at MP2/6-31G(d,p), 6-31G(2p,2d), B1 6-31G(2d,2p) and MPW91/6-31G(2d,2p) levels shows that the calculated results were in reasonable agreement with experimental result (Jose *et al.,*). Density functional theory was used to propose the reasonable mechanism of decomposition of 2-methoxy-1-chloroethane, 3--methoxy-1-chloropropane and 4-methoxy-1-

chlorobutane. It was discovered that 2-methoxy-1-chloroethane and 3--methoxy-1-chloropropane proceeds through a concerted non-synchronous four centered cyclic transition state to give olefin while 4-methoxy-1-chlorobutane proceeds through a five-membered transition state(Brea *et al.,* 2012).

2. Computational Procedure

Conformational search was carried out on the structure using molecular mechanics force field (MMFF) which is quite successful in assigning low energy conformers and in providing quantitative estimates of conformational energy differences (Warren, 2003) to obtain the structure with the lowest energy value which is an indication of the stability of the molecule. Geometry optimization was performed on the ground state (GS), the transition state (TS) and the products to obtain the geometric parameters such as bond length, bond angle, dihedral, bond order and atomic charges, the data obtained were used to calculate the other thermodynamics parameters. H_{11} is the hydrogen atom to be eliminated.

Reaction path calculations were performed on the optimized geometry of the isopropyl bromide under study using $H_{11} - Br_6$ as the reaction coordinate. The internal coordinate was varied from its initial distance of 3.765$\mathring{A}$ in the stable reactants form to its value 1.20$\mathring{A}$ in the product molecule. This inter atomic distance is slowly altered throughout the reaction path calculation taking the value from 3.765 (initial value) to 1.20 Angstroms its approximate value in the stable product molecule in 20 steps.

Using the guess-transition state in Spartan on the suggested mechanism, the transition state structure was optimized and was subjected to the two tests needs to be performed in order to verify that a practical geometry corresponds to a saddle point (transition structure) and that this saddle point corresponds to the reactants and products. The tests are:

That the Hessian matrix of second – energy derivations with respect to coordinates yields one and only one imaginary frequency which will be in the range of 400-2000 cm^{-1} and the normal coordinates corresponds to the imaginary frequency smoothly corrects reactants and products. This could be achieved by animating the normal coordinate. The intrinsic reaction coordinates method was also used by optimizing the molecule subject to a fixed position along the reaction coordinate (Warren, 2003). The transition state was confirmed using the IRC method. Two IRC calculations were performed. The first one a positive perturbation was done by an initial perturbation on the atomic coordinates in the direction of the single negative frequency while the other one a negative perturbation performed along the same normal coordinates.

Thermodynamic calculations were obtained for isopropyl bromide through calculation on the ground state GS, Transition TS and the product. The statistical mechanically calculated enthalpy and entropy were used which is not the true representative of the total energy of the molecule, knowing that the large portion of the enthalpy in a molecule is contained in its bonds and physical conformation hence the sum of the ground state energy (GSE) and the statistical mechanically calculated enthalpy are used to arrive at a closer approximation of the true energy of the molecule. With the said modified version of the heat of reaction the equation is given as shown below (Spartan Guide to calculations).The enthalpy of a species will be defined as:

$$H_i = GSE_i + H_i^{sm} \quad (1)$$

Where the superscript 'sm' is the statistical mechanically calculated enthalpy. Substitute this into the initial definition of the heat of reaction we have:

$$\Delta H_{Rxn} = \left(GSE_{product} + H^{sm}_{Product}\right) - \left(GSE_{reactant} + H^{sm}_{reactants}\right) \quad (2)$$

The enthalpy of reaction was calculated at 623K.

Activation energy (Ea) was calculated according to the transition state theory for a unimolecular reaction at 623K.

$$Ea = \Delta H + RT \quad (3)$$

The entropy of the reaction was calculated by taking the difference of product and reactant entropies that is

$$\Delta S_{reaction} = S_{Product} - S_{reactants} \quad (4)$$

The Gibbs free energy was calculated using the modified version of the heat of reaction equation. Knowing that

$$G = H - TS$$

$$\Delta G^{*} = \Delta H^{*} - T\Delta S. \quad (5)$$

The first order coefficient k (T) was calculated using transition State theory (TST) Benson and O' Neal, 1967 assuming that the transition coefficient is unity as shown in the following equation

$$k(T) = \frac{K_B' T}{h} \exp\left[\frac{-\Delta G^{*}}{RT}\right] \quad (6)$$

Where $\Delta G^{\neq}$ is the Gibbs free energy change between the reactant and the transition state and K' and h are the Boltzmann and Planck's constants respectively.

Arrhenius rate equation is given as

$$k(T) = \frac{K_B{}' T}{h} \exp\left[\frac{-Ea}{RT}\right]$$ [Benson and O' Neal, 1976] (7)

3. Result And Discussion

3.1 Geometry Optimization

Isopropyl bromide has only one conformer and the energy is 2.708kJmol^{-1}. Geometry optimization was performed on the ground state (GS), the transition state (TS) and the products to obtain the geometric parameters such as bond length, bond angle, dihedral, bond order and atomic charges, the data obtained were used to calculate the other thermodynamics parameters. H_{11} is the hydrogen atom to be eliminated. Bond length and atomic charges are shown in Tables 1 and 2.

3.2 Reaction Path Studies

As reported in previous work, (Mclever *et a.,l* 1971) instead of the energy to pass smoothly through a maximum, it rose to a very high value and the geometry suddenly drop to a product with a drop in the heat of formation with the values approximately the same as the sum of the expected products (hydrogen bromide and propene) as shown in Fig 2:

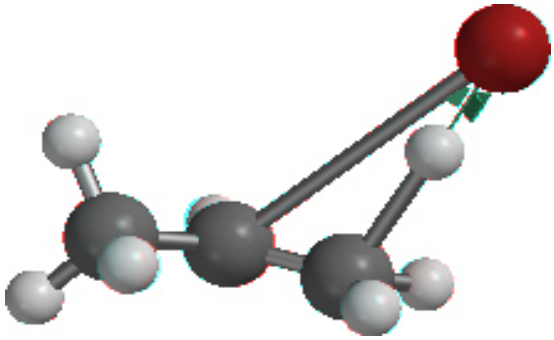


Fig 2: Reaction Path Study

3.3 Transition state

Potential energy surfaces provide a basis for understanding the relationship between molecular structures and stability. Stable molecules correspond to energy minima along the reaction coordinate. Transition states correspond to the energy maxima. However, the underlying principle is that stable molecules (energy minima) will be interconnected by smooth pathway passing through well – defined transition state. The plot of energy in (kJ/mol) against the intrinsic reaction coordinate to ascertain the transition state is as shown in Fig 3. The mechanism follows Markovnikov's addition reaction; the transition state (TS) was confirmed by the single negative Eigen value in the Hessian matrix, intrinsic reaction coordinate and by only one imaginary IR value at absorption band 931cm^{-1} with the intensity at 472.96.

3.4 Atomic Charges

Atomic charges are shown in Mulliken. The Mulliken charges are preferred because it gives simple and reasonable estimates of atomic charges. (Warren, 2003) charges in the TS: (Table 1), show that H_4 (+0.279, +0.308 and +0.247) has the largest charge development while Br_{11} (-0.680, -0.788 and -0.561) has the least as reported by (Lee ., 1987) and the bond polarization in the $C_4 - Br_6$ is in the direction of $C_4^{\delta+}$------- $Br_6^{\delta-}$ and is the rate determining step.

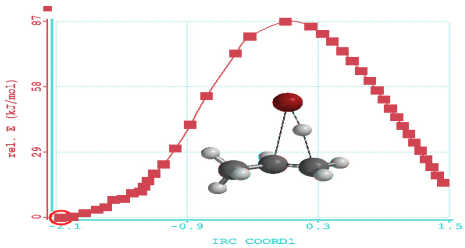


Fig 3: A plot to show the intrinsic reaction coordinates

3.5 Calculations

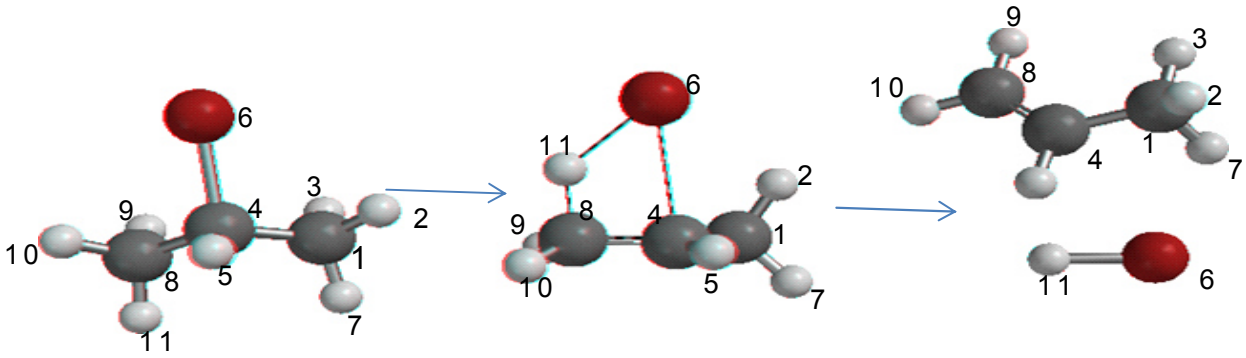


Fig 4: Reactant, Transition State and Products of Isopropyl Bromide

Table 1: Bond Length for the reactant, transition state and products

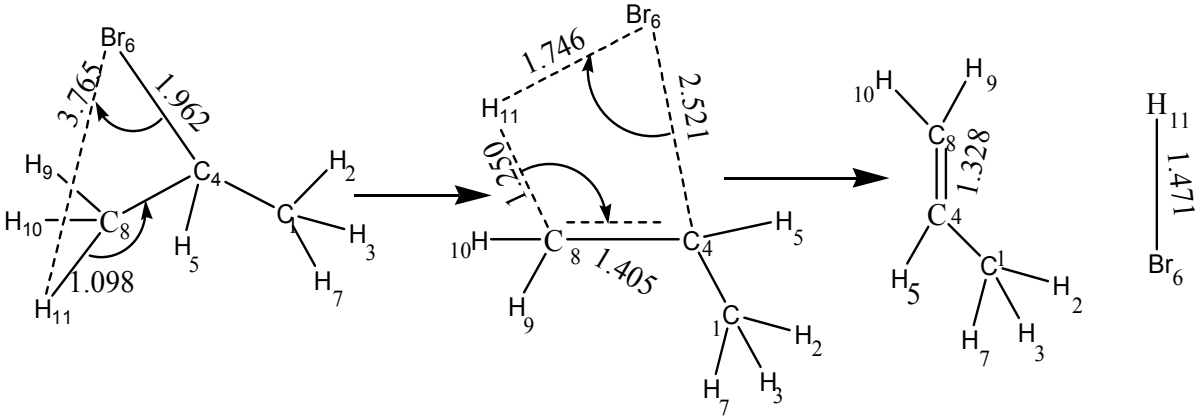
Bond		**PM3**	**HF/6-31G**	**DFT/B3LYP/6-31G***
C_1-H_2	GS	1.098	1.087	1.095
	TS	1.098	1.085	1.094
	PRD	1.098	1.086	1.099
C_1-H_3	GS	1.097	1.084	1.093
	TS	1.103	1.080	1.097
	PRD	1.098	1.087	1.099
C_1-C_4	GS	1.495	1.520	1.521
	TS	1.468	1.473	1.497
	PRD	1.480	1.502	1.502
C_1-H_7	GS	1.098	1.082	1.098
	TS	1.099	1.090	1.100
	PRD	1.098	1.084	1.095
C_4-H_5	GS	1.110	1.079	1.092
	TS	1.100	1.076	1.092
	PRD	1.097	1.079	1.091
C_4-Br_6	GS	1.962	1.985	2.013
	TS	2.521	3.227	3.227
	PRD	-	-	-
C_4-C_8	GS	1.495	1.520	1.521
	TS	1.405	1.397	1.340
	PRD	1.328	1.321	1.333
C_8-H_9	GS	1.098	1.082	1.095
	TS	1.093	1.078	1.088
	PRD	1.087	1.076	1.087
C_8-H_{10}	GS	1.097	1.084	1.093
	TS	1.093	1.077	1.117
	PRD	1.086	1.077	1.089
C_8-H_{11}	GS	1.098	1.087	1.098
	TS	1.250	1.187	1.090
	PRD	-	-	-
H_{11}-Br_6	GS	3.765	3.021	3.883
	TS	1.746	2.165	1.438
	PRD	1.471	1.417	1.433

Table 2: Atomic charges for the reactant, transition state and products

Atoms	State	PM3	HF	DFT
H_1	GS	+0.063	+0.185	+0.168
	TS	+0.112	+0.220	+0.193
	PRD	+0.082	+0.204	+0.142
	Δq=TS-GS	+0.049	+0.035	+0.025
C_2	GS	-0.317	-0.480	-0.440
	TS	-0.338	-0.577	-0.510
	PRD	-0.154	-0.228	-0.340
	Δq=TS-GS	-0.021	-0.097	-0.07
H_3	GS	+0.053	+0.171	+0.153
	TS	+0.108	+0.225	+0.206
	PRD	+0.083	-0.417	+0.138
	Δq=TS-GS	+0.055	+0.054	+0.053
H_4	GS	+0.062	+0.192	+0.172
	TS	+0.279	+0.308	+0.247
	PRD	-0.147	+0.185	+0.192
	Δq=TS-GS	+0.217	+0.116	+0.075
C_5	GS	+0.005	-0.209	-0.150
	TS	+0.279	+0.101	+0.067
	PRD	-0.150	+0.181	-0.045
	Δq=TS-GS	+0.274	+0.310	+0.217
H_6	GS	+0.084	+0.217	+0.185
	TS	+0.318	+0.300	+0.226
	PRD	+0.098	-0.131	+0.125
	Δq=TS-GS	+0.234	+0.083	+0.041
C_7	GS	-0.137	-0.480	-0.440
	TS	+0.104	-0.599	-0.492
	PRD	-0.067	+0.188	-0.484
	Δq=TS-GS	+0.241	-0.119	-0.052
H_8	GS	+0.053	+0.171	+0.153
	TS	+0.078	+0.243	+0.196
	PRD	+0.051	-0.516	+0.157
	Δq=TS-GS	+0.025	+0.072	+0.043
H_9	GS	+0.062	+0.185	+0.168
	TS	+0.126	+0.309	+0.204
	PRD	+0.032	+0.178	+0.154
	Δq=TS-GS	+0.064	+0.124	+0.036
H_{10}	GS	+0.062	+0.192	+0.172
	TS	+0.073	+0.258	+0.224
	PRD	+0.045	+0.178	+0.154
	Δq=TS-GS	+0.028	+0.066	+0.052
Br_{11}	GS	-0.168	-0.146	-0.143
	TS	-0.680	-0.788	-0.561
	PRD	-0.167	+0.177	-0.193
	Δq=TS-GS	-0.512	-0.642	-0.418

3.6 *Mechanism of decomposition of ethyl bromide*

The gas-phase elimination reaction of isopropyl bromide proceeds thorough a four centered mechanism suggesting C_4 – Br_6 (2.521 Å) as the rate determining step. In the transition state, the C_8-H_{11} (1.250 Å) is stretched, become long and virtually broken while the H_{11}-Br_6 is almost fully formed as shown in scheme1.



Scheme 1: Mechanism of pyrolysis of Isopropyl bromide

Table 3: Arrhenius and Thermodynamic parameters at 623k

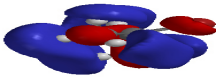
METHOD	Ea (kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol.k)	ΔG(kJ/mol)	Log A	k (s^{-1})	Ref
EXPERIMENTAL	199.99	194.81	N/A	N/A	13.6	2.4 X 10^{-4}	O'Neal &Benson (1967)
PM3	192.42	187.24	9.91	203.92	13.6	3.1 X 10^{-3}	
HF/6-31G*	191.85	185.42	15.74	175.45	13.9	7.6 X 10^{-3}	
DFT/B3LYP/6-31G*	190.80	185.62	13.44	199.22	13.8	6.6 X 10^{-3}	

Kinetic and thermodynamic calculations at 623k for semi-empirical PM3, HF/6-31G* and DFT/B3LYP6-31G* as shown in Table 3 for PM3 Ea(192.43), ΔH(194.82), ΔG (203.92), (log A(13.6) and k(3.1 X 10^{-3}) and with DFT/B3LYP6-31G* Ea(190.80), ΔH (185.62) log A (13.4) ΔG (199.22), log A 13.8 and k(6.6 X 10^{-3}) against experimental result with Ea (199.99), ΔH(194.82) and log A 13.6 are in perfect agreement.

Table 4: Homo and Lumo Energy

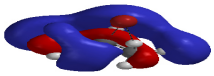
ENERGY		PM3	HF/6-31G*	DFT/B3LYP/6-31G*
E HOMO	GS	-12.13	-10.68	-7.36
	TS	-9.55	-0.842	-0.68
	PRD	-22.23	-10.14	-15.18
E LUMO	GS	-0.19	4.17	-0.20
	TS	-1.90	0.34	-0.77
	PRD	0.99	4.37	-1.03

Interaction between two atomic orbitals give rise to two new orbitals and one of the new orbitals has higher energy than the original (anti-bonding orbital) and the lower one (bonding orbital). The HOMO, LUMO energy characterizes the ability of electron accepting (Madhavan *et al*., 2011) When one of the initial orbitals is filled with a pair of electrons (a Lewis base) and the outer is empty (a Lewis acid), the two electrons can thus be placed in the lower level of the two new orbitals. This Filled-Empty interaction has a stabilizing effect. The HOMO and LUMO energy as shown in Table 4 for semi-empirical PM3 method is E-HOMO (eV) for GS (-12.13), TS (-9.55) and PRD (-22.25), for HF/6-31G* GS(-10.68) TS(-8.42) and PRD(-10.14) for DFT/B3LYP/6-31G* GS (-7.36) TS (-0.68), PDR (15.18) and the E-LUMO for PM3, GS (-0.19), TS(-1.90) and PRD (0.99), HF/6-31G*GS(4.17)TS(0.34) and PRD (4.37), DFT/B3LYP/6-31G* GS (-0.20) TS (-0.77), PDR (1.03).



LUMO REACTANT

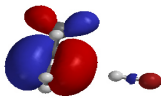
HOMO REACTANT



LUMO TS

HOMO TS

LUMO PRODUCT



HOMO PRODUCT

Fig 5: HOMO/LUMO density Surface diagram for the reactant, transition state and products of Isopropyl bromide

Fig 5 shows the HOMO and LUMO for the reactant, transition state and the products. The colour blue represents the maximum value of LUMO and the red colour represents the minimum value. The red regions on the density surface indicate the areas where electrons can easily be removed (ionization), these areas are subject to electrophilic attack, but at the blue regions, ionization is relatively very difficult. (Hehre and Ohlinger, 2010). The IR values obtained theoretically as shown in Table 5 compares favourably well with experimental (*www.chem.ucla.edu/~webspectra/irtable.html)* values for instance the $\upsilon(C\text{-}H)_{str\ sp^2}$ (3100 – 3010cm^{-1}), $\upsilon(C\text{-}H)_{str\ sp^3}$ (2950 – 2850 cm^{-1}), obtained theoretically against experimental results $\upsilon(C\text{-}H)_{str\ sp^2}$ (2966 cm^{-1}) for the reactant and for the products $\upsilon(C{=}C)_{str}$ (1862 cm^{-1}), $\upsilon(C\text{-}H)_{str\ sp^2}$ (3021-3156 cm^{-1}) and $\upsilon(H\text{-}Br)_{str}$ (2439 cm^{-1}) against experimental values of $\upsilon(C{=}C)_{str}$ (1680 - 1620 cm^{-1}), $\upsilon(C\text{-}H)_{str\ sp^2}$ (3100 - 3010 cm^{-1}) with the corresponding IR spectra shown in Fig 5.

Table 5: Infra-Red (cm^{-1})

	EXPERIMENTAL	CALCULATED
REACTANT $\upsilon(C\text{-}H)_{bend}$ $\upsilon(C\text{-}H)_{str\ sp^2}$ $\upsilon(C\text{-}H)_{str\ sp^3}$	 N/A 3100 – 3010 2950 - 2850	 1030 - 1408 2966 3079 – 3176
PRODUCT1 (ETHENE) $\upsilon(C\text{-}H)_{bend}$ $\upsilon(C{=}C)_{str}$ $\upsilon(C\text{-}H)_{str\ sp^2, sp^3}$	 N/A 1680 - 1620 3100 - 3010	 1004 – 1440 1862 3021-3156
PRODUCT 2 (HBr) $\upsilon(H\text{-}Br)_{str}$	 N/A	 2439

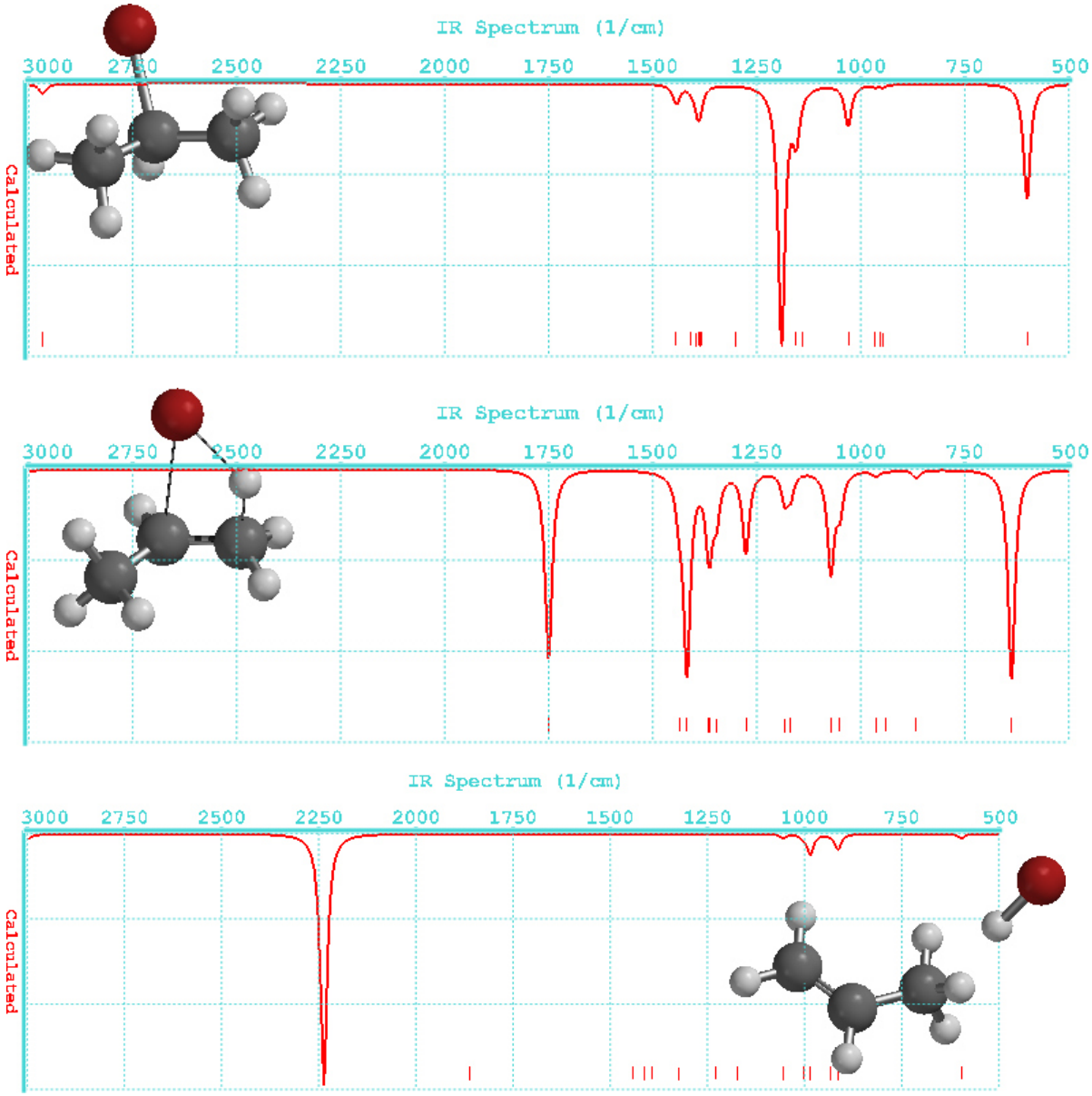


Fig 7: IR Spectra for the Reactant, Transition state and Products of Isopropyl Bromide

4. Conclusion

It is observed that both semi-empirical and *ab-initio* method could effectively predict the kinetics, mechanism and thermodynamics of the gas-phase pyrolysis of isopropyl bromide Also, the computed Arrhenius parameters obtained at 623 kelvin are in perfect agreement with experimental values.

Refrences

Adejoro, I. A. and Bamkole, O. T. (2009) Kinetics and Mechanism of elimination of ethyl acetate in the gas phase: A theoretical study. African Journal of Pure and Applied Chemistry. 3 (7).

Adejoro, I.A. and Emmanuel Ekeh (2010) Theoretical Study of the Kinetics of the Pyrolytic Elimination Reaction of Ethyl Chloride. E- Journal of Chemistry 7(1): 271 – 274.

Benson, S.W. A and O'Neal, H. E. (1967) Method for estimating the Arrhenius A factor for four and Six – Center Unimolecular Reactions. Journal of Physical Chemistry 71 (9): 2911.

Brea, O., Loroño, M., Marquez, E., Mora, J. R., Cordova, T. and Chuchani, G. (2012), Theoretical study of methoxy group influence in the gas-phase elimination kinetics of methoxyalkyl chlorides. Int. J. Quantum Chem., 112: 2504–2514

Brusco, Y., Berroteran, N., Loroño, M., Córdova, T. and Chuchani, G. (2009), Theoretical calculations for neighboring group participation in gas-phase elimination kinetics of 2-hydroxyphenethyl chloride and 2-methoxyphenethyl chloride. J. Phys. Org. Chem., 22: 1022–1029

Ikchoon L.,Young S., Park Y. S., Bon-Su L (1987) Determination of reactivity by MO Theory (Part 50). MO studies on the Gas Phase Pyrolysis of Ethers, Bull, Korean Chem.Soc.8 (3) 193 -196.
Infrared spectroscopy correlation table – Wikipedia, the free encyclopedia.
IR Absorption Table. *www.chem.ucla.edu/~webspectra/irtable.html*
Jose R. Rojas, Marcos Lorono, Jose, R. Mora, Rosa, M. Dominguez, Tania Cordova and Gabriel Chuchani (2009) Theoretical studies of the gas-phase pyrolysis kinetics of ω-bromonitriles, ZCH_2CH_2Br [Z=NC, $NCCNH_2$, $NCCH_2CH_2$, Int. J, Chem, Kinet; 41:168-175.
Madhhavan J. Arulmozhi, S, and Victor Anthony Raj (2011) HOMO, LUMO analysis and first order hyperpolarizability of 2-amino-5-chlorobenzophenone using computational methods. Pelagia Research Library Der Chemica 2(6): 158-163
McIver J.W. Jr. and A. Kormonicki, (1971) Rapid Geometry Optimization for Semi- Empirical Molecular Orbital Methods. *Chem. Phys. Letts. 10:* 303.
Romero, M. L., Cordova, T. and Chuchani, G. (2009), Theoretical study of neighboring group participation of methyl ω-chloroesters elimination kinetics in the gas phase. J. Phys. Org. Chem., 22: 403–409
Spartan Calculation Guide. www.engin.umich.edu/~cre/web_mod/quantum/topic03.htm
Warren Hehre and Sean Ohlinger (2010) Spartan User guide for Windows, Machintosh and Linux. Wavefunction. Inc USA. 45
Tania, Cordova, Alexandra, Rotinov and Gabriel Chuchani. (2004) Experimental and theoretical study of the homogenous, unimolecular gas-phase elimination kinetics of methyl oxalyl chloride. Journal of Physical Organic Chemistry Wiley InterScience (www.interscience.wiley.com). 17: 148-151.
Warren Hehre and Sean Ohlinger Spartan '10 Tutorial and user's guide. Wavefunction 2010 Inc. ISBN978-1-890661-41-4
Warren J. Henhre (2003) A Guide to molecular Mechanics and Quantum Chemical Calculations. Irvine USA : 399.

The IISTE is a pioneer in the Open-Access hosting service and academic event management. The aim of the firm is Accelerating Global Knowledge Sharing.

More information about the firm can be found on the homepage:
http://www.iiste.org

CALL FOR JOURNAL PAPERS

There are more than 30 peer-reviewed academic journals hosted under the hosting platform.

Prospective authors of journals can find the submission instruction on the following page: http://www.iiste.org/journals/ All the journals articles are available online to the readers all over the world without financial, legal, or technical barriers other than those inseparable from gaining access to the internet itself. Paper version of the journals is also available upon request of readers and authors.

MORE RESOURCES

Book publication information: http://www.iiste.org/book/

IISTE Knowledge Sharing Partners

EBSCO, Index Copernicus, Ulrich's Periodicals Directory, JournalTOCS, PKP Open Archives Harvester, Bielefeld Academic Search Engine, Elektronische Zeitschriftenbibliothek EZB, Open J-Gate, OCLC WorldCat, Universe Digtial Library , NewJour, Google Scholar